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Spatial and Temporal Trends in Short-chain
Chlorinated Paraffins in Lake Ontario Sediments
By:
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Abstract

Short-chain chlorinated paraffins (polychlorinated-[C_{10} – C_{13}]-n-alkanes) were measured in Lake Ontario sediments collected during a lake-wide survey to characterize spatial and temporal trends in contamination. The Lake Ontario average SCCP sediment concentration was 49 ng/g, which was somewhat higher than the lake-wide average for ΣDDT (32 ng/g). Individual stations in each of the depositional basins exhibited the highest concentrations, ranging from 147 ng/g (dry wt.) to 410 ng/g at an index station in the Niagara (western) basin. Relative average contributions of the carbon chain groups to total SCCPs on a lake-wide basis were as follows: ΣC_{10} = 24%, ΣC_{11} = 35%, ΣC_{12} = 34%, ΣC_{13} = 6.6%. Assessment of core profiles and estimates of SCCP fluxes indicated that the western end of Lake Ontario is more heavily impacted (SCCP flux of 170 μg/m^2 yr), and potentially influenced by local industrial sources of SCCPs. Maximum accumulation of SCCPs in the western basin occurred in the mid-1970s. In contrast, SCCP concentrations in a core from the central area of the lake (SCCP flux of 8.0 μg/m^2 yr) were more similar to levels characteristic of remote locations primarily impacted by atmospheric sources.

Tendances spatiales et temporelles des paraffines chlorées à chaîne courte dans les sédiments du lac Ontario

C.H. Marvin, S. Painter, G.T. Tomy, G.A. Stern, E. Braekevelt et D.C.G. Muir

Résumé

Dans le cadre d'un relevé portant sur l'ensemble du lac Ontario, nous avons prélevé des sédiments et mesuré le taux de paraffines chlorées à chaîne courte (n-alcanes C10-13 polychlorés) afin de déterminer les tendances spatiales et temporelles de ces contaminants. Le taux moyen de PCCC des sédiments du lac Ontario était de 49 ng/g, ce qui est un peu supérieur au taux moyen de Σ DDT mesuré à l'échelle du lac (32 ng/g). Certaines stations de chacun des bassins de sédimentation présentaient les concentrations les plus élevées, allant de 147 ng/g (poids sec) à 410 ng/g à une station de référence du bassin ouest (Niagara). À l'échelle du lac, les contributions moyennes relatives des différentes chaînes carbonées aux PCCC totales étaient de : $\Sigma C_{10} = 24$ %, $\Sigma C_{11} = 35$ %, $\Sigma C_{12} = 34$ % et $\Sigma C_{13} = 6,6$ %. L'évaluation du profil des carottes et les flux estimatifs de PCCC révèlent que la contamination est la plus sévère à l'extrémité ouest du lac Ontario (flux de PCCC de 170 $\mu g/m^2$ par année); les sources de PCCC seraient dans ce cas-ci des industries locales. Dans le bassin ouest, l'accumulation maximale de PCCC s'est produite au milieu des années 70. Par contre, dans une carotte prélevée au centre du lac, les concentrations de PCCC (flux de CPPP de 8,0 $\mu g/m^2$ par année) se rapprochaient davantage des niveaux caractéristiques des localités éloignées, qui sont touchées principalement par des sources atmosphériques.

NWRI RESEARCH SUMMARY

Plain language title
Contaminants Associated with Suspended Sediments in Lakes Erie and Ontario, 1997 - 2000.

What is the problem and what do sicentists already know about it?
Presence of contaminants in bottom sediments are a primary sink for contaminants in the Great Lakes, and can be a primary source to higher trophic levels potentially resulting in deleterious health impacts on fish and wildlife. Recent bottom sediment surevys conducted throughout the Great Lakes have resulted in a resonable understanding of spatial distributions and temporal trends in a range of contaminant classes, including PCBs, OCs and metals.

Why did NWRI do this study?
The Great Lakes Sediment Assessment Program is currently assessing changes in sediment quality throughout the Great Lakes since earlier Departmental surveys conducted in the late 1960s and early 1970s. Information from this program is important to the understanding of the anthropogenic activities on open lake environments, and allows assessment of changes in contaminant concentrations since the advent of measures to reduce sources and loadings. Although there is now a reasonable understanding of trends in conventional contaminants, there is a paucity of information on the distribution and fate of a number of compound classes of new and emerging concern chemicals, including short-chain chlorinated paraffins.

What were the results?
Short-chain chlorinated paraffins (polychlorinated-[C10 – C13]-n-alkanes) were measured in Lake Ontario sediments collected during a lake-wide survey to characterize spatial and temporal trends in contamination. The Lake Ontario average SCCP sediment concentration was 49 ng/g, which was somewhat higher than the lake-wide average for SDDT (32 ng/g). Individual stations in each of the depositional basins exhibited the highest concentrations, ranging from 147 ng/g (dry wt.) to 410 ng/g at an index station in the Niagara (western) basin. Assessment of core profiles and estimates of SCCP fluxes indicated that the western end of Lake Ontario is more heavily impacted, and potentially influenced by local industrial sources of SCCPs. Maximum accumulation of SCCPs in the western basin occurred in the mid-1970s. In contrast, SCCP concentrations in a core from the central area of the lake were more similar to levels characteristic of remote locations primarily impacted by atmospheric sources.

How will these results be used?
These results will contribute to the decision-making process within binational initiatives, primarily the GLBTS, in order to select candidate contaminant classes for further long-term monitoring and research.

Who were our main partners in the study?
Ontario Region, DFO

Sommaire des recherches de l'INRE

Titre en langage clair
Contaminants associés aux sédiments en suspension dans les lacs Érié et Ontario, de 1997 à 2000.

Quel est le problème et que savent les chercheurs à ce sujet?
Les contaminants présents dans les sédiments du fond forment un puits primaire de contaminants dans les Grands Lacs et peuvent constituer une source primaire pour les niveaux trophiques supérieurs, occasionnant ainsi des problèmes de santé chez les poissons et les autres espèces sauvages. Des relevés récents des sédiments de fond menés à l'échelle des Grands Lacs ont permis de comprendre assez bien les tendances spatiales et temporelles d'une gamme de contaminants, notamment les BPC, les OC ainsi que certains métaux.

Pourquoi l'INRE a-t-il effectué cette étude?
Le programme d'évaluation des sédiments des Grands Lacs évalue actuellement les changements survenus dans la qualité des sédiments à l'échelle des Grands Lacs depuis les relevés effectués par le Ministère à la fin des années 60 et au début des années 70. Ce programme fournira des informations importantes pour la compréhension de l'effet des activités humaines sur le milieu pélagique lacustre et permettra d'évaluer les changements survenus dans la concentration des contaminants depuis l'établissement de mesures visant à réduire les sources et les charges. Aujourd'hui, bien que nous ayons une bonne compréhension de l'évolution des contaminants classiques, il nous manque de l'information sur la distribution et le sort d'un certain nombre de classes de composés qui sont nouveaux ou commencent à soulever des inquiétudes, notamment les paraffines chlorées à chaîne courte.

Quels sont les résultats?
Dans le cadre d'un relevé portant sur l'ensemble du lac Ontario, nous avons prélevé des sédiments et mesuré le taux de paraffines chlorées à chaîne courte (n-alcanes C10-13 polychlorés) afin de déterminer les tendances spatiales et temporelles de ces contaminants. Le taux moyen de PCCC des sédiments du lac Ontario était de 49 ng/g, ce qui est un peu supérieur au taux moyen de Σ DDT mesuré à l'échelle du lac (32 ng/g). Certaines stations de chacun des bassins de sédimentation présentaient les concentrations les plus élevées, allant de 147 ng/g (poids sec) à 410 ng/g à une station de référence du bassin ouest (Niagara). L'évaluation du profil des carottes et les flux estimatifs de PCCC révèlent que la contamination est la plus sévère à l'extrémité ouest du lac Ontario; les sources de PCCC seraient dans ce cas-ci des industries locales. Dans le bassin ouest, l'accumulation maximale de PCCC s'est produite au milieu des années 70. Par contre, dans une carotte prélevée au centre du lac, les concentrations de PCCC (flux de PCCC de 8,0 $\mu g/m^2$ par année) se rapprochaient davantage des niveaux caractéristiques des localités éloignées, qui sont touchées principalement par des sources atmosphériques.

Comment ces résultats seront-ils utilisés?
Ces résultats faciliteront la prise de décisions dans le cadre des initiatives binationales, principalement le GLBTS, qui sélectionne des classes candidates de contaminants pour la recherche et le suivi à long terme.

Quels étaient nos principaux partenaires dans cette étude?
Région de l'Ontario, MPO

Spatial and Temporal Trends in Short-Chain Chlorinated Paraffins in Lake Ontario Sediments

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Abstract

Short-chain chlorinated paraffins (polychlorinated-[C_{10} – C_{13}]-n-alkanes) were measured in Lake Ontario sediments collected during a lake-wide survey to characterize spatial and temporal trends in contamination. The Lake Ontario average SCCP sediment concentration was 49 ng/g, which was somewhat higher than the lake-wide average for ΣDDT (32 ng/g). Individual stations in each of the depositional basins exhibited the highest concentrations, ranging from 147 ng/g (dry wt.) to 410 ng/g at an index station in the Niagara (western) basin. Relative average contributions of the carbon chain groups to total SCCPs on a lake-wide basis were as follows: $\Sigma C_{10} = 24\%$, $\Sigma C_{11} = 35\%$, $\Sigma C_{12} = 34\%$, $\Sigma C_{13} = 6.6\%$. Assessment of core profiles and estimates of SCCP fluxes indicated that the western end of Lake Ontario is more heavily impacted (SCCP flux of 170 μg/m^2 yr), and potentially influenced by local industrial sources of SCCPs. Maximum accumulation of SCCPs in the western basin occurred in the mid-1970s. In contrast, SCCP concentrations in a core from the central area of the lake (SCCP flux of 8.0 μg/m^2 yr) were more similar to levels characteristic of remote locations primarily impacted by atmospheric sources.

Key Words: Lake Ontario, short-chain chlorinated paraffins, polychlorinated-*n*-alkanes, sediment, persistent organic pollutants

Introduction

Environment Canada, together with collaborating agencies, conducts Great Lakes sediment surveys to measure the occurrence and spatial distribution of environmental

contaminants. Historical surveys in Lake Ontario were conducted in the late 1960's and early 1970's to characterize the spatial extent of surficial sediment contamination by a variety of contaminants including metals [1], polychlorinated biphenyls (PCBs) and organochlorine pesticides [2], mercury [3] and mirex [4]. In addition, the historical impact of human activities was assessed using sediment cores [1,2,5]; levels of metals including total mercury and lead were compared to pre-colonial concentrations. In 1998, 66 stations previously sampled in a 1968 survey, were re-sampled for surficial sediments and sediment cores in order to undertake a comprehensive suite of analyses for assessment of contemporary sediment contamination, and to investigate temporal changes [6]. In addition, the analyte suite incorporated compound classes of widely used but rarely determined chlorinated chemicals, including short-chain chlorinated paraffins (SCCPs).

Commercially produced SCCPs are polychlorinated-[C_{10} to C_{13}]-n-alkanes (PCAs) with chlorine content typically ranging from 40% to 50% by mass. Commercial PCAs are classified according to carbon chain length: $C_{10} - C_{13}$ (short-chain), $C_{14} - C_{17}$ (medium-chain, MCCPs) and $C_{20} - C_{30}$ (long-chain). These compounds, also known by the industrial name of chlorinated paraffins (CPs), are used primarily as extreme temperature additives in metal working fluids for a variety of engineering and metal working operations such as drilling, machining/cutting, drawing and stamping [7-9]. These compounds are also used as additives in paints and sealants, flame-retardants and plasticizers. SCCPs have been produced since 1930 with steady increases in consumption. Global production of SCCPs in the late 1990s was estimated at approximately 50 kt [10]; consumption of SCCPs in the United States in the mid-1990s was approximately 18 kt/yr [8], which represented roughly 20% of total PCA production. The United States EPA has placed SCCPs on the Toxic Release Inventory (TRI, www.epa.gov/tri/), and in Canada they are classified as Priority Toxic Substances under the Canadian Environmental Protection Act due to carcinogenicity in rats and mice, and their potential for bioaccumulation and persistence in the environment. SCCPs releases to the US environment reported under the TRI were 18 t in 1995 based on reports from 63 use facilities, most of which were located in states within the Great Lakes basin. Most releases were to air (85%), probably from mists created during metalworking. The SCCPs not accounted for under the TRI were possibly sorbed onto solids and landfilled or incinerated.

As a result of their hydrophobicity, SCCPs should be bioaccumulated predominantly through food chain transfer [11]. Chlorinated paraffins are readily accumulated from food by fish in laboratory experiments, although accumulation is influenced by carbon chain length and chlorine content [12,13]. SCCPs with greater than 60% chlorine were found to have equilibrium biomagnification factors (BMFs) > 1 and half-lives ≥ 50 days in juvenile rainbow trout, which implies a potential to biomagnify in aquatic food chains [12,14]. When compared to the half-lives in rainbow trout for a series of non-metabolizable PCB congeners (i.e. 2,4,2',4'-substituted), a series of synthetic C_{10}-C_{16}-PCAs exhibited intermediate behaviour [14,15]. Most SCCP congeners had lower half-lives and BMFs than PCB congeners with the same Log K_{ow}, but some highly chlorinated components had similar half-lives. Tomy et al. (16) measured levels of SCCPs in marine mammals from the Arctic and the St. Lawrence River estuary. Total SCCP concentrations in blubber of beluga whales, ringed seals and walruses ranged from 0.164 µg/g to 1.4 µg/g. Concentrations of SCCPs were higher in beluga blubber from the St. Lawrence estuary than for Arctic beluga, and SCCP profiles had higher proportions of longer carbon chain length higher percent chlorinated congeners, which was indicative of contamination from local sources. SCCPs in Arctic mammals showed a predominance of shorter carbon chain length compounds, which was consistent with contamination as a result of long-range transport. Bennie et al. (17) determined levels of both SCCPs and MCCPs in beluga from the St. Lawrence River, and rainbow trout and carp from western Lake Ontario.

Concentrations of SCCPs have been measured in water, sediment, air and biota over the past 20 years and were recently reviewed [18,19]. SCCPs were determined in sediments in remote lakes in Canada in order to investigate local sources and long-range transport potential [20]. This study found detectable levels of SCCPs in all of the sediment cores, with the highest levels near urban areas. There is limited information for SCCPs in sediment and biota in the Great Lakes, and studies in the watershed generally have been limited to surveys by the US EPA [21] and Environment Canada [17,22]. However, these studies used low-resolution mass spectrometry for analysis of SCCPs, and consequently suffered relatively high detection limits and low specificity, especially for individual homologs and carbon chain groups within the SCCP group of compounds. Tomy et al. [23] reported SCCPs in sediments, fish and zebra mussels in a limited number of samples from the mouth of the Detroit River using high resolution MS. Muir

et al. [10] measured SCCPs in sediments from Canadian harbours in Lake Otario. In this study, we have examined the spatial distribution and temporal trends of C_{10}-C_{13} PCAs in Lake Ontario sediments using both surficial samples and box cores to assess temporal SCCP accumulation.

Material and Methods

Sampling

Sediment samples were collected from 66 stations in Lake Ontario (Figure 1) in 1998 using a mini box core procedure, of which a subset of 25 samples was analyzed for SCCPs. Samples consisted of fine-grained sediments classified as glacio-lacustrine clay, sand, silt or mud. The top 3 cm of the sediment was sub-sampled for analyses of POPs and placed in pre-rinsed glass jars. Sediment cores were obtained from index stations in the Niagara Basin (station 1007, 43°26'01"N; 79°24'00"W) and Mississauga Basin (station 1034, 43°34'39"N; 78°11'58"W) of Lake Ontario aboard the CCGS Limnos in June 1998 using a box corer. The Mississauga Basin cores (7 cm dia) were sectioned on board ship in 1 cm increments from the surface to 16 cm, and every two cm thereafter to the bottom of the core and placed in pre-rinsed glass jars. The Niagara Basin box cores (10 cm dia) were sectioned on board ship into 0.5 cm slices (0-5 cm) and 1 cm slices (5-30 cm) and stored in plastic WhirlPak polyethylene bags. All samples were frozen for transport to the laboratory. Both cores were dated using a ^{210}Pb technique [24,25] based on the Constant Rate of Supply model of Oldfield and Appleby [26].

Extraction and Analysis

Internal standards of 1,3-dibromobenzene, endrin ketone, PCB 30 and PCB 204 were added to sediment samples prior to extraction. Sections from the Niagara Basin core were centrifuged to remove excess water, mixed with sodium sulfate, and extracted with dichloromethane (DCM) using an accelerated solvent extractor (ASE, Dionex Instruments). Surficial sediments and sections from the Mississauga Basin box core (10-15 g) were freeze-dried and extracted in dichloromethane using the ASE. Solvent extracts were evaporated, exchanged into hexane, and separated into three fractions of increasing polarity on Florisil (8 g; 1.2 % v/w water deactivated). The first fraction (F1) was eluted with hexane and contained PCBs, p,p'-DDE, *trans*-nonachlor, mirex and a small portion of the toxaphene congeners. The eluate was treated with activated copper powder to remove elemental sulfur, followed by addition

of aldrin for volume correction. F1 was subjected to an additional alumina (1 g activated) column fractionation during which SCCPs were separated from PCBs by eluting the column with 1% diethyl ether hexane followed by 50% diethyl ether hexane.

The SCCPs were quantified using high-resolution gas chromatography/electron capture negative ionization/high-resolution mass spectrometry (HRGC-ECNI-HRMS) as described by Tomy et al. [23]. In brief, analyses were performed on a 5890 Series II gas chromatograph (Hewlett-Packard Instruments), fitted with a DB-5ms fused silica column (30 m x 0.25 mm i.d., 0.25 um film thickness), connected to a Kratos Concept MS (EBE geometry, Kratos Instruments Manchester UK) controlled by a Mach 3 data system. Analyses were performed in SIM mode at a resolving power of ~12 000 (sufficient to exclude potential interferences from other organochlorines), with a cycle time of 1 sec for each window, and equal dwell times for each ion monitored.

Quality Assurance

SCCPs may be present in commercial products and in machined metal parts, therefore, steps were taken to reduce possible contamination in the field and laboratory. Procedural blanks with all reagents were analysed for SCCPs with each batch of samples. Glassware, glass fibre filters and sodium sulfate were solvent rinsed and heated at 450°C prior to use. Sediment coring equipment was rinsed with hexane and acetone prior to use. A slice dated to pre-1900 from the Niagara Basin sediment core was also analyzed to examine possible contamination from sample collection and handling. In general levels of SCCPs in procedural blanks were low or non-detect. Internal standards recoveries were generally >75%; no corrections were made for recoveries. Procedural blanks were run with every 10 sediment samples. Method detection limits (MDL) were calculated for total SCCPs (ΣSCCPs), *i.e.*, mean plus 3 SD in the background signals from procedural blanks was estimated at 7 ng/g (*n=4*).

Results and Discussion

Sediment Distribution in Lake Ontario

An understanding of the sedimentology of the Great Lakes is in turn fundamental to understanding spatial distributions of POPs in sediments. Modern sediments of the Great Lakes reflect the post-glacial history of the area. For the purposes of discussing trends in sediment

contamination as they related to sediment distribution and transport processes, we adopted the convention for Lake Ontario sediment characterization described by Thomas et al. [27]. Presently, the general sedimentology of the Great Lakes is characterized by continued deposition of fine clayey sediments in deep-water areas over older deposits that include glaciolacustrine clays, tills and glacial features. Glacial moraines segregate areas of Lake Ontario into three individual depositional basins (Figure 1). Sediments are classified either as non-depositional, consisting of bedrock, glacial till and glaciolacustrine clay, or depositional, consisting of fine-grained postglacial muds comprised mostly of material in the silt and clay particle size ranges. Non-depositional sediments including bedrock and till are found predominantly in nearshore areas, and are overstepped in turn by the glaciolacustine clays moving offshore into the areas of postglacial muds that correspond to the deep-water depositional basins. Lake Ontario is divided into three major depositional areas; the Niagara Basin was separated from the Mississauga Basin by the Whitby – Olcott Sill, and the Scotch – Bonnet Sill separated the Mississauga Basin from the Rochester Basin (Figure 1). At the outflow of Lake Ontario into the St. Lawrence River, the Kingston Basin experiences reduced sediment transport from the main lake due to the presence of a major topographical barrier, the Duck – Galloo Sill.

Short-Chain Chlorinated Paraffins in Surficial Sediments

SCCPs were detected in all 26 surficial sediment samples from Lake Ontario. Agreement between duplicate sediment samples was good with relative percent deviations averaging 26%, for ΣSCCPs. The lake-wide average ΣSCCP surficial sediment concentration was 49 ng/g dry wt., which was somewhat higher than the lake-wide average of 32 ng/g dry wt. for ΣDDT, and roughly half the lake-wide average of 100 ng/g dry wt. for total PCBs [6]. Individual stations in the Niagara basin (410 ng/g dry wt.), Mississauga Basin (154 ng/g dry wt.) and Rochester Basin (147 ng/g dry wt.) exhibited the highest SCCP surficial sediment SCCP concentrations. As a result of the more limited sampling frequency, compared to other POPs such as PCBs [6], the distribution of SCCPs did not exhibit a definitive spatial trend (Figure 2). The highest concentrations of other compound classes in Lake Ontario sediments, including PCBs, were observed within the deep-water depositional areas of the three major lake basins [6]. The predominant circulation pattern in Lake Ontario resembles a counterclockwise gyre [28] that can

result in hydrophopic contaminants, associated primarily with suspended particulate material in the water column, being uniformly distributed on a lake-wide basis.

Relative average percent contributions (±SD) of the carbon chain groups to ΣSCCPs on a lake-wide basis were as follows: ΣC_{10} = 24 ±5.0%, ΣC_{11} = 35 ±4.3%, ΣC_{12} = 34 ±4.8%, ΣC_{13} = 6.6 ±3.5%. The averaged profile of the SCCP homolog and carbon chain groups representing all of the Lake Ontario surficial sediment samples (Figure 3) was compared with profiles of Lake Ontario water [29], and PCA-60, a commercial CP mixture of $C_{10} - C_{13}$ carbon chain lengths and approximately 60% chlorine by mass [23]. Differences in the relative contributions of SCCP homologs and carbon chain lengths may reflect different sources of SCCPs, as well as variations in the extent of degradation of SCCPs in sediment. The trend in relative abundances of the homologs within the individual carbon chain groups were similar among all three profiles, with the exception of the higher $C_{12}C_{18}$ contribution in surface water, and the higher $C_{11}C_{16}$ contribution in the PCA-60 technical mixture. The individual carbon chain SDs corresponded to relative percent SDs of 21.6%, 12.3%, 14.1% and 47.3%, respectively. The relative SDs for the C_{10}, C_{11} and C_{12} carbon chains were low, which evidenced consistency on a lake-wide basis. However, the C_{13} carbon chain exhibited a higher level of variation (47.3% RSD), and a range of percent relative contributions to individual station total SCCP levels of 2.9% to 20%. A comparison of the Lake Ontario averaged SCCP profile with those reported by Muir et al. [10] for sediments collected from embayments and tributary outflows in proximity to highly industrialized/urbanized areas are shown in Figure 4. The Lake Ontario averaged sediment profile was quite similar to samples collected in areas that receive discharges from primarily urban residential areas (Humber River and Port Credit). The other three sample sites shown in Figure 4 were in areas more heavily impacted by both urban and industrial activities (Hamilton Harbour and Toronto Harbour). The most dramatic differences in the profiles was related to the C_{13} carbon chain; sample profiles attributed to the primary influence of urban residential activities, including the Lake Ontario composite profile, had lesser (roughly 5%) contributions from the C_{13} carbon chain while contributions in samples influenced by industrial activities ranged from 17% - 44% (Figure 4).

Muir et al. [29] also observed relatively high C_{13} carbon chain contributions (roughly 40%) in sections of cores sampled downstream of a MCCP manufacturing facility. Therefore,

the relatively high C_{13} contributions imply a presence due partially to the manufacturing of the $C_{14} - C_{17}$ compounds; the MCCPs have applications common to SCCPs, in addition to uses in paints, caulkings and PVC plastics. These comparisons showed that the averaged Lake Ontario sediment profile was indicative of general urban residential activity, however, many individual sites exhibited much higher relative C_{13} contributions indicating that SCCP contamination in Lake Ontario was predominately due to a combination of urban residential and industrial activity. In addition, high SCCP concentrations at three stations in the open lake, and the relatively high lake-wide average concentration (49 ng/g dry wt.), indicated the presence of significant local sources.

The highest Lake Ontario surficial sediment ΣSCCP concentrations, ranging from 147 ng/g dry wt. to 410 ng/g dry wt., were similar to concentrations in surface slices in a core from the southern basin of Lake Winnipeg (135 ng/g), which is an area reported to be potentially primarily contaminated by local sources [20]. There is limited data for sediment levels of SCCPs in the Laurentian Great Lakes; Tomy et al. [23] reported a ΣSCCP value of 288 ng/g dry wt. for a sediment sample from the Detroit River. The Lake Ontario lake-wide average ΣSCCP concentration of 49 ng/g was much higher than sediment concentrations reported for lakes influenced primarily by atmospheric sources [20]. In addition, the Lake Ontario SCCP profiles were not dominated by the lower chlorine, lower chain length congeners to an extent indicative of mainly atmospheric sources [20]. The less chlorinated, lower chain length congeners are reported to be the more volatile components of commercial SCCP mixtures [30,31] and are predominant in areas influenced primarily by long-range atmospheric transport. The spatial pattern in surficial sediment SCCP contamination in Lake Ontario sediment was presumably an indication of the influence of both historical and present day urban and industrial activities. The highest ΣSCCP concentrations were associated with depositional areas in the major basins characterized by fine-grained depositional sediment distributions as described by Thomas et al. [27]. The major lake basins are characterized by sediments dominated by fine-grain silts and clays that adsorb contaminants more effectively compared to sediments dominated by sands, hence the observed spatial patterns of contaminants may not have been only a function of primary sediment transport pathways and proximity to sources, but also substrate type.

Short-Chain Chlorinated Paraffins in Sediment Cores

Two sediment cores from Lake Ontario were analyzed for SCCPs in order to assess depositional trends, to study historical profiles and fluxes of SCCPs, and to investigate the extent of potential *in situ* degradation. The SCCP core profiles from the Niagara Basin (station 1007, Figure 1) and Mississauga Basin (station 1034) are shown in Figure 5. The total SCCP concentration in the top 1 cm section (410 ng/g dry wt) from the core at station 1007 (Niagara basin) was the highest observed in Lake Ontario surficial sediments. This relatively high concentration indicated that SCCPs are present in the western depositional areas of the lake at similar or higher concentrations than some harbours and embayments [10]. However, the surficial concentration of the core at station 1034 (Mississauga basin) in the central depositional area of the lake was roughly 20-fold lower (19 ng/g dry wt.). The higher concentrations of SCCPs in the surficial sections of the Niagara basin core, compared to the Mississauga basin core, were also reflected in the trend reported for surface water contamination. Muir et al. [10] reported a surface water concentration of 1,750 ng/m^3 in the Niagara basin, compared to 420 ng/m^3 in the Mississauga basin (Muir, unpubl. data). The higher concentrations of SCCPs in the western end of Lake Ontario may be due to the proximity to a large urban/industrial area, and the influence of tributaries including the Niagara River. There is a considerable body of literature that implicates the Niagara River as a primary source or vector for many contaminants in Lake Ontario. In contrast to other Great Lakes such as Lake Superior, Lake Ontario is greatly impacted by contaminant sources other than atmospheric deposition. Thompson et al. [32] estimated that the Niagara River constitutes two-thirds of the total loadings of contaminants including PCBs and lead. Other studies [33-37] have identified the Niagara River as a primary source of chlorinated organic contaminants, including PCBs, in Lake Ontario.

Levels of SCCPs determined in surficial sediments and cores from the Lake Ontario study were compared with data from studies of other Canadian lakes. Surficial sections of cores from Lake Winnipeg, Lake Nipigon, Lake Fox, and Hazen Lake exhibited concentrations ranging from 10-to 250 ng/g dry wt. [20]. Concentrations of total PCAs in surface sediments declined substantially from mid-latitude areas including the southern basin of Lake Winnipeg (135 ng/g dry wt., 50°N/96°W, Manitoba), to 4.52 ng/g in Hazen Lake (high Arctic); corresponding surficial sediment fluxes were 147 μg/m^2/yr and 0.9 μg/m^2/yr, respectively. The relatively high

flux of PCAs to the south Lake Winnipeg basin indicated a local source of contamination. A surficial flux of PCAs to Fox Lake (61°N/135°W), a sub-arctic lake in the Yukon, was also high (34 $\mu g/m^2/yr$). Significantly lower fluxes were measured in Lake Nipigon (49°N/89°W, N. Ontario), 3 $\mu g/m^2/yr$, the northern basin of Lake Winnipeg (52°N/98°W, Manitoba), 4 $\mu g/m^2/yr$ and to Ya-Ya Lake (69°N/134°W, Arctic) 0.45 $\mu g/m^2/yr$. The remote locations of Hazen and Ya-Ya Lakes, and the low levels of PCAs observed in sediment cores at these sites, were consistent with long-range atmospheric transport as the primary source. The SCCP fluxes for Lake Ontario sediments were estimated using sedimentation rates derived from ^{210}Pb dating analyses of the two cores [24,25]. Assessment of the SCCP flux estimates for the Lake Ontario cores indicated local sources of contamination influenced the Niagara basin (station 1007, 170 $\mu g/m^2$ yr), while the surficial flux for the Mississauga basin core (station 1034, 8.0 $\mu g/m^2$ yr) were more similar to those reported for the remote lakes.

  The profiles of PCAs in the mid-continental lakes showed maxima in core sections dated from the early 1980's to the 1990's, while profiles of ΣDDT showed maxima in the 1960's [20]. In contrast, the core profile from the Niagara basin (station 1007) showed maximum accumulation of SCCPs in the period of the late 1960's to the early 1970s (Figure 5). However, the surficial concentration (410 ng/g dry wt.) was half of the maximum value (820 ng/g dry wt.) determined in a section dated to approximately 1970. The SCCP core profile for the Niagara basin core was similar to that of other POPs, including dioxins and furans [38]. Correspondingly, contamination of Lake Ontario from the Niagara River watershed has been substantially reduced from levels in the 1960s [37]. Wong et al. [39] reported that accumulation rates for a variety of POPs during the mid-1990s were 15 – 30% of the peak accumulation rates, but had remained relatively constant since the early-to mid-1980s. Any trend in the SCCP profile from the Mississauga basin (station 1034) core was difficult to determine, due to very low levels in many of the core sections approaching the MDL. However, assessment of the SCCP levels at station 1034 based on core sections exhibiting SCCP concentrations >10 ng/g dry wt. indicated a trend toward increasing concentrations over the period of the 1960's to the late 1990's. Profiles of other POPs in cores from station 1034, including PCBs and dioxins and furans, were markedly different from SCCPs in that peak concentrations occurred in the 1960s – 1970s followed substantial declines [6,38].

Variations in SCCP carbon chain lengths and homolog profiles with depth are shown in core sections corresponding to dates of 1949, 1971 and 1996 at station 1007 in the Niagara basin (Figure 6). There was a trend toward increasing contributions of the C_{13} toward the top of the core. The high total SCCP concentrations in the station 1007 core, and the high relative contributions of the C_{13} carbon chain, both indicated a strong influence of industrial activity as a primary source in this area of Lake Ontario. Significant increases in the contribution of the C_{13} carbon chain were observed in core sections corresponding to 1964 and 1982, which corresponded to substantial increases and decreases, respectively, in total SCCPs concentrations in the core. There was a similar trend toward an increasing contribution of the C_{13} carbon chain in the station 1034 core, but the percent contribution in the surficial section was only 1.5%, which was more representative of a SCCP profile reflecting urban residential activity in the watershed, or contamination arising from air deposition as a result of long-range transport. In concert with the observed enrichment in the longer carbon chains with decreased depth in the core, there were also apparent variations in the homolog profiles with depth (Figure 7). There was a trend toward increased levels of lower chlorinated congeners within the carbon chain groups at increasing depth in the core. This observation could be the result of a dechlorination mechanism in more recent sediments, or a shift in industrial usage or manufacturing patterns in favor of heavier chlorinated SCCP technical mixtures.

In summary, the presence of SCCPs appears to be widespread in Lake Ontario sediments. The highest levels of SCCP contamination were associated with fine-grained sediments within the major lake depositional basins, while stations more characteristic of inshore environments exhibited relatively lower contaminant levels. This spatial trend was potentially influenced by urban and industrial activities in the watersheds and along major tributaries. Hydrophobic contaminants associated with sediments originating in the tributary watersheds are ultimately deposited in the depositional basin areas of Lake Ontario. Individual stations in each of the three major depositional basins exhibited the highest surficial sediment concentrations, ranging from 150 ng/g dry wt. to 410 ng/g dry wt at an index station in the Niagara basin. The Lake Ontario average SCCP sediment concentration was 49 ng/g, which is well above levels characteristic of remote lake areas impacted solely by atmospheric deposition. This relatively high mean concentration, coupled with the assessment of core profiles and SCCP fluxes from the Niagara

and Mississauga basins of the lake, implicated urban industrialized areas of the western shoreline as potential significant local sources of SCCPs on a lake-wide basis. However, the western basin core profile also indicated that current SCCP levels in surficial sediments correspond to a roughly 50% reduction from peak levels of contamination in the 1970's.

The results of this study also indicate that the contribution of the C_{13} carbon chain to the total SCCP burden may be indicative of primary sources in Lake Ontario. Some stations in nearshore areas exhibited relatively low C_{13} carbon chain contributions, and exhibited total SCCP profiles similar to samples representative of urban residential areas. Other stations exhibited high C_{13} carbon chain contributions, and SCCP profiles more indicative of samples from highly industrialized areas. However, most Lake Ontario samples exhibited profiles intermediate in nature, and potentially reflect a combination of source contributions including heavy industry, urban residential areas, and atmospheric deposition as a result of long-range transport. The increases in the relative concentration of the C_{13} carbon chain in cores analyzed in the study, and particularly from the Niagara basin, may be related to the primary source of SCCPs, or differences in degradation rates. The enrichment in C_{13} may also have resulted partially from manufacturing and subsequent applications involving MCCPs.

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Figure Captions:

Figure 1. Map of Lake Ontario showing sampling stations and major depositional areas.

Figure 2. Spatial distribution of C_{10}-C_{13} short-chain chlorinated paraffins (ng/g) in Lake Ontario surifical sediments.

Figure 3. Mean percent contributions of individual C_{10}-C_{13} short-chain chlorinated paraffin homolog and carbon chain groups in surficial sediments of Lake Ontario, and a corresponding profile in a surface water sample. The numbers 5 to 9 of each chain length group (C_{10}-C_{13}) represent the penta- to nonachloro-substituted compounds determined by ECNI-HRMS. Water data supplied by Muir (unpubl. data). Data for the PCA-60 technical mixture was taken from Tomy et al. [23].
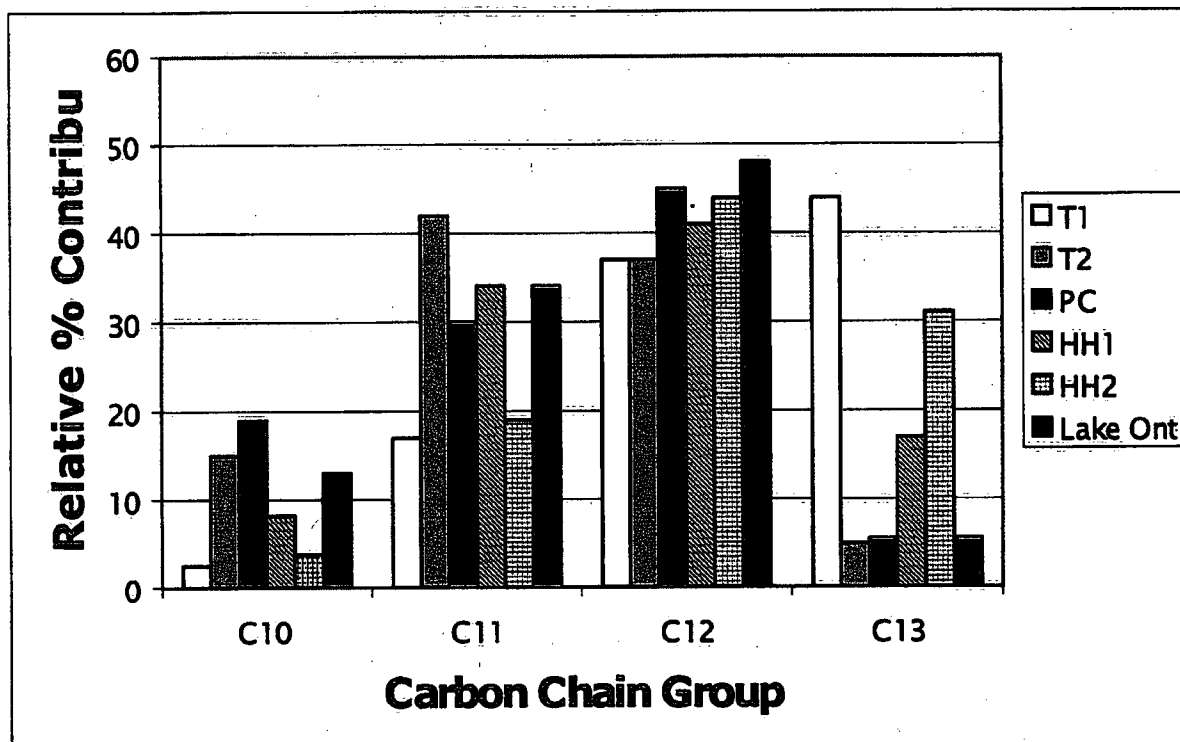
Figure 4. Comparisons of mean percent relative contributions of individual C_{10}-C_{13} short-chain chlorinated paraffin homolog and carbon chain groups in surficial sediments from areas of Lake Ontario. The numbers 5 to 9 of each chain length group (C_{10}-C_{13}) represent the penta- to nonachloro-substituted compounds determined by ECNI-HRMS. T1 denotes Toronto Harbour; T2 denotes Humber River (Toronto); PC denotes Port Credit (near Toronto); HH1 denotes the western area of Hamilton Harbour; HH2 denotes the Windermere Basin area of Hamilton Harbour, and; Lake Ont denotes the lake-wide average profile of the 25 Lake Ontario sediment samples. Data for samples other than Lake Ontario surficial sediments taken from Muir et al. [10].

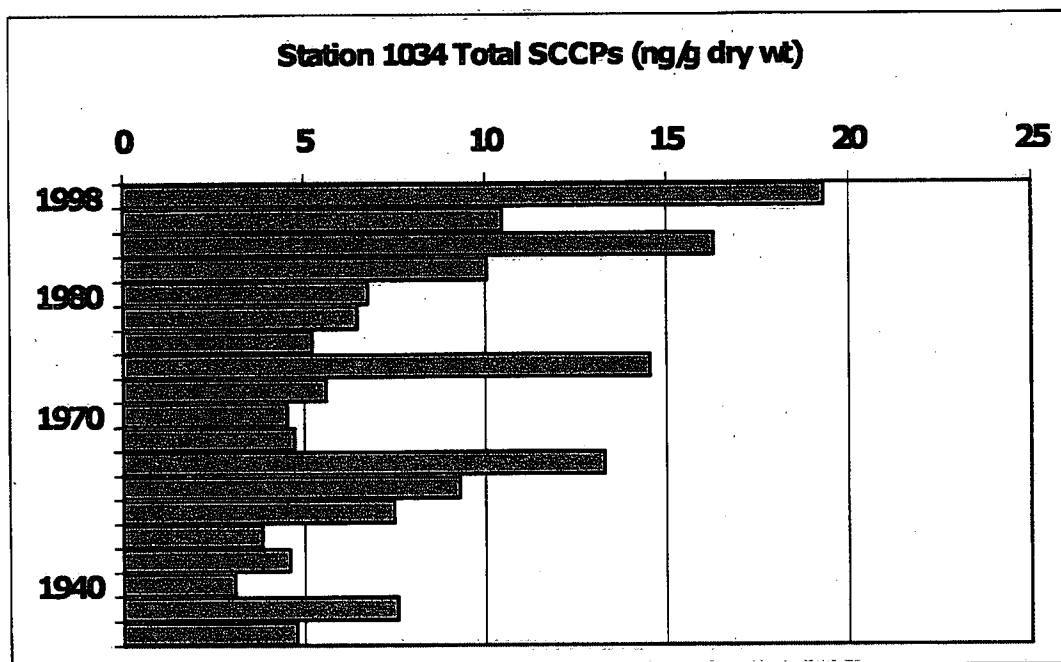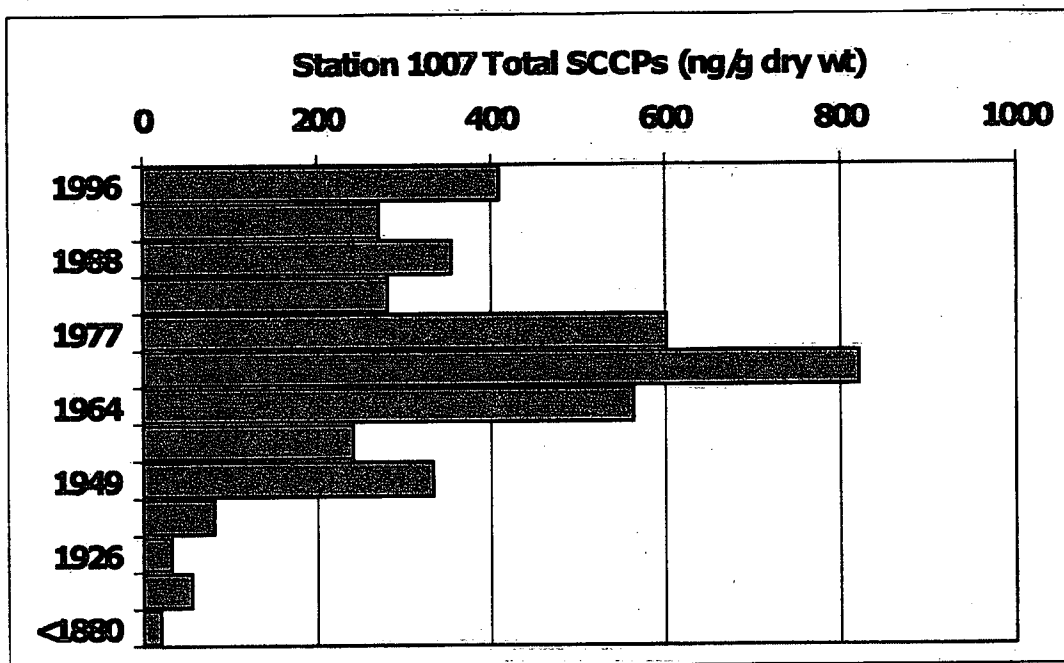**Figure 5.** Concentration profiles (ng/g dry wt.) of total C_{10}-C_{13} short-chain chlorinated paraffins in dated sediment cores from the Niagara Basin (station 1007) and Mississauga Basin (station 1034) of Lake Ontario.

Figure 6. Variation in C_{10}-C_{13} short-chain chlorinated paraffin carbon chain abundances with depth in sediment core slices from the Niagara Basin (station 1007) of Lake Ontario.

Figure 7. Percent contributions of C_{10}-C_{13} short-chain chlorinated paraffin homologs and carbon chain groups in a core from the Niagara Basin (station 1007, Figure 1) of Lake Ontario. The numbers 5 to 9 of each carbon chain length group (C_{10}-C_{13}) represent the penta- to nonachloro-substituted compounds as determined by ECNI-HRMS.
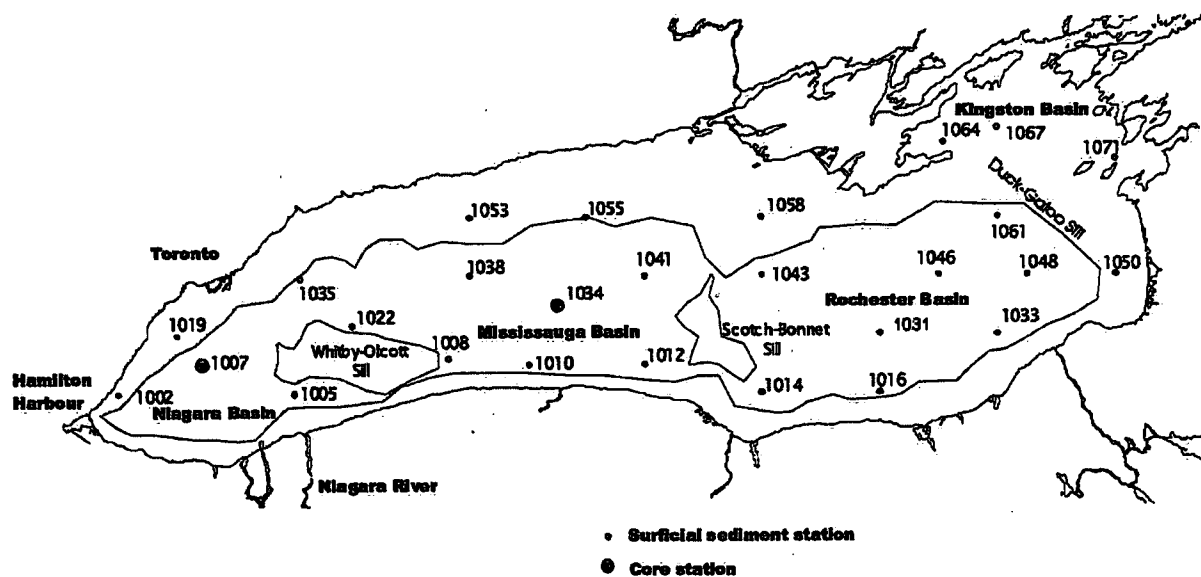
Figure 1. Map of Lake Ontario showing sampling stations and major depositional areas.
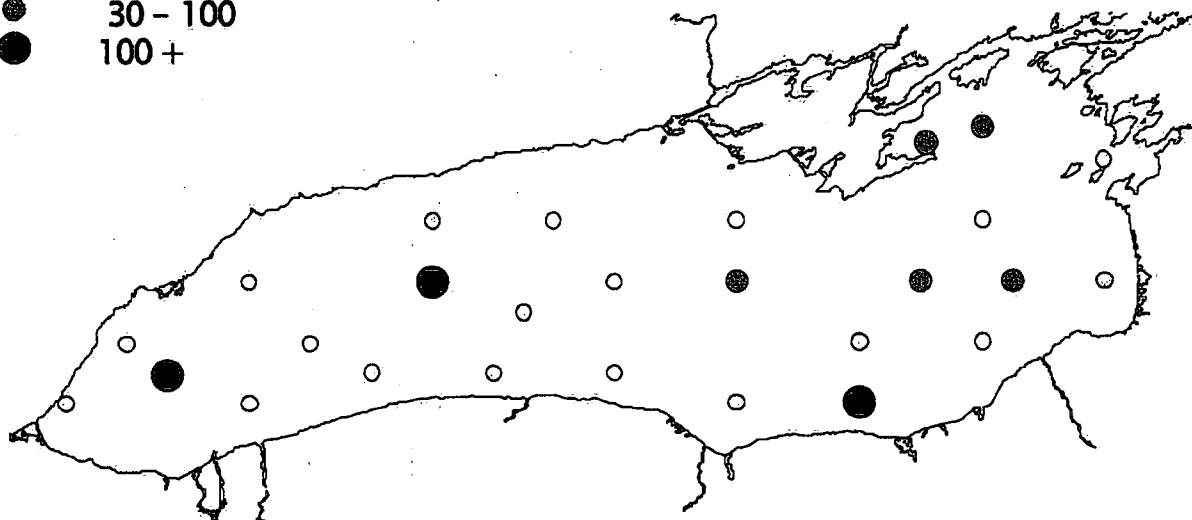
Figure 2. Distribution of C_{10}-C_{13} short-chain chlorinated paraffins (ng/g dry wt.) in Lake Ontario surifical sediments in 1998.

Sediment
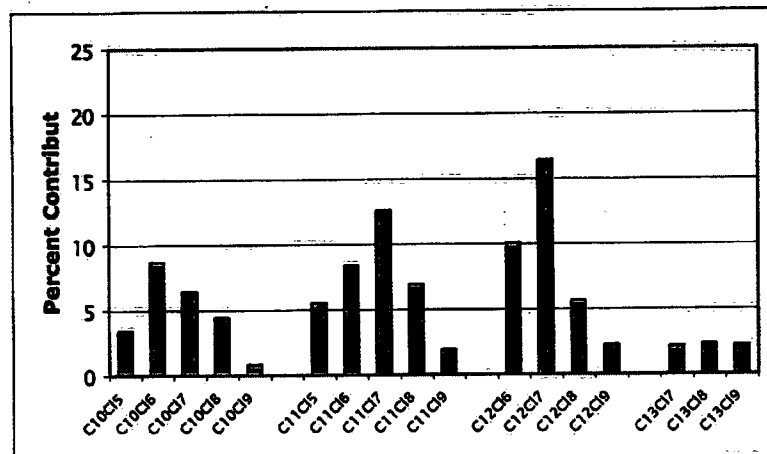
Water
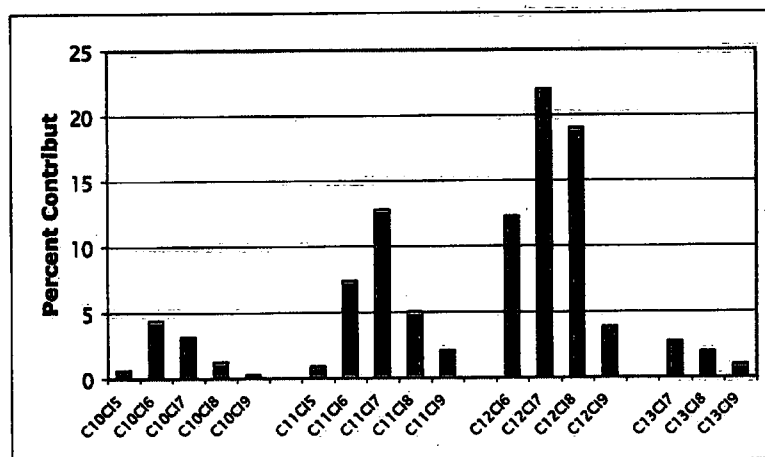
PCA-60
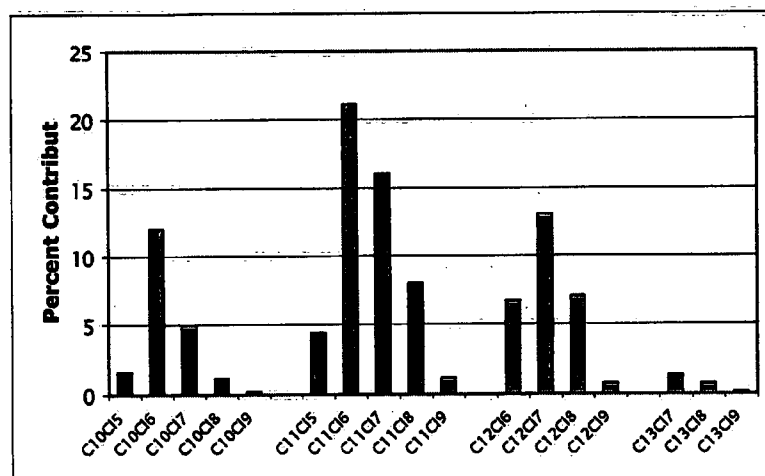
Figure 3. Mean percent contributions of individual SCCP homolog and carbon chain groups in surficial sediments of Lake Ontario, and a corresponding profile in a surface water sample. The numbers 5 to 9 of each chain length group (C_{10}-C_{13}) represent the penta- to nonachloro-substituted compounds determined by ECNI-HRMS. Water data supplied by Muir (unpubl. data). Data for the PCA-60 technical mixture was taken from Tomy et al. [23].

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Figure 5. Concentration profiles (ng/g dry wt.) of ΣSCCPs in dated sediment cores from the Niagara Basin (station 1007) and Mississauga Basin (station 1034) of Lake Ontario.
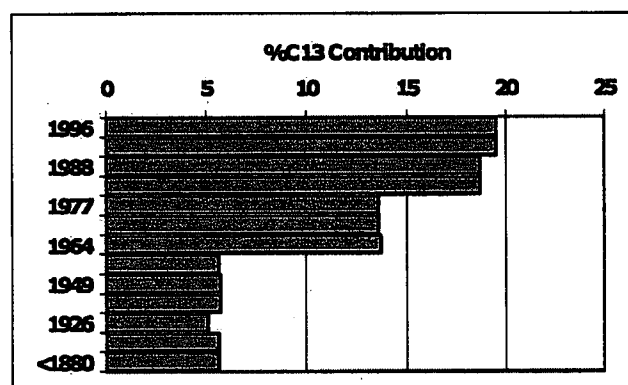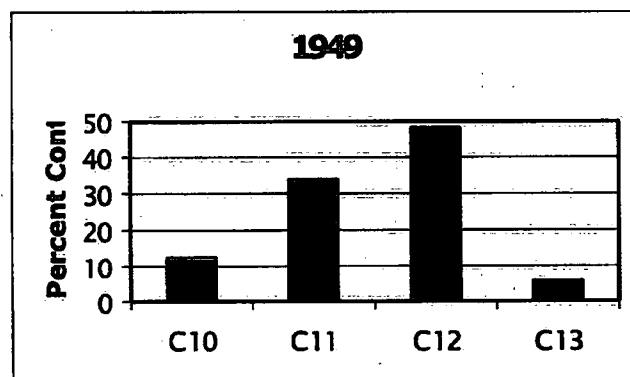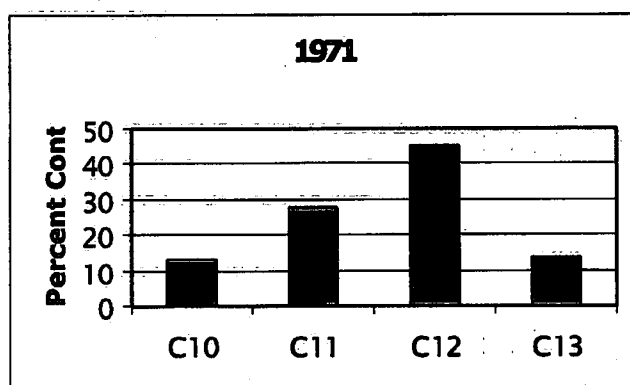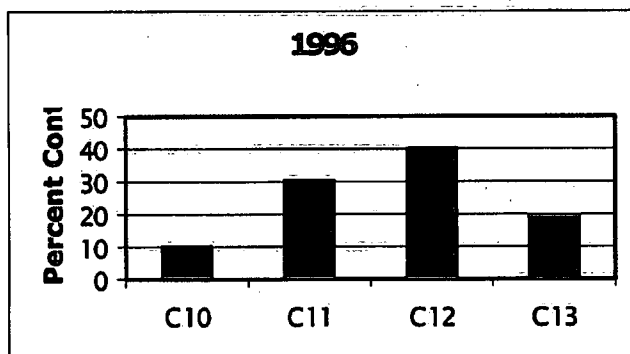
Figure 6. Variation in carbon chain length abundances with depth in sediment core slices from the Niagara Basin (station 1007) of Lake Ontario, and percent contribution of the C_{13} carbon chain with depth.
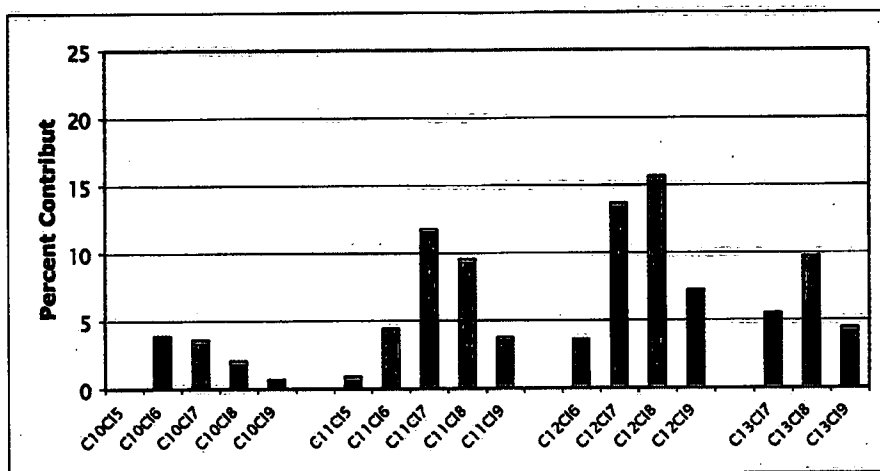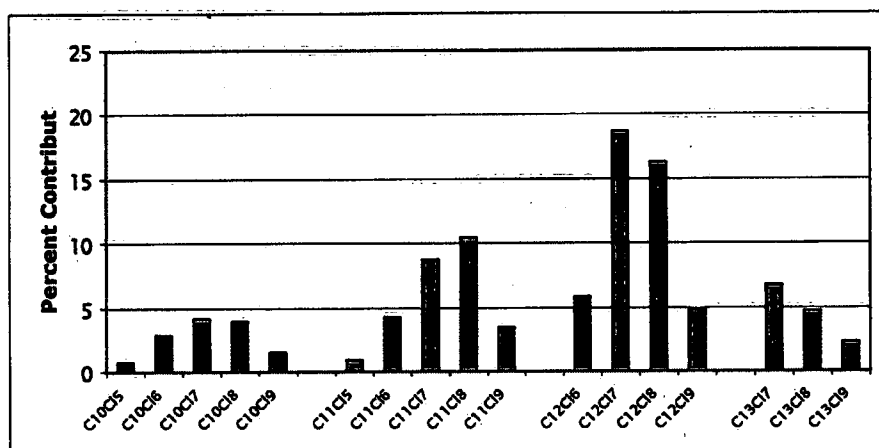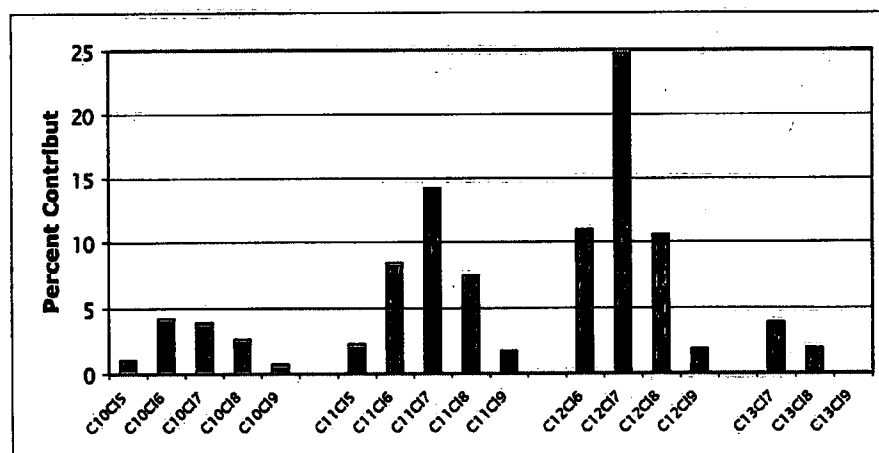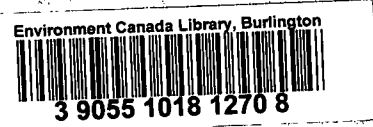
1996

1971

1949

Figure 7. Percent contributions of SCCP homologs and carbon chain groups in a core from the Niagara Basin (station 1007) of Lake Ontario. The numbers 5 to 9 of each chain length group (C_{10}-C_{13}) represent the penta- to nonachloro-substituted compounds determined by ECNI-HRMS.
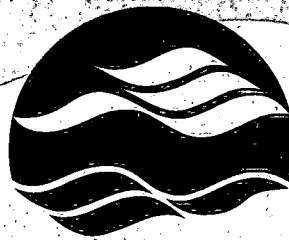
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